

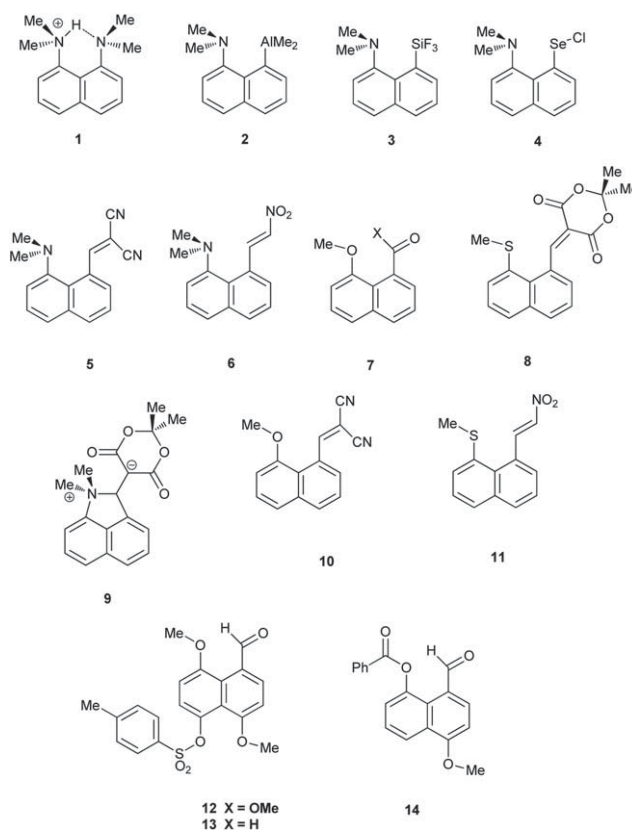
The use of the triptycene framework for observing $O\cdots C=O$ molecular interactions†

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The triptycene skeleton has been used to measure (1,5) interactions between aldehyde groups, placed at both sp^3 centres, and hydroxy or methoxy groups, placed at the respective *ortho* position on a benzene ring; $HO\cdots CHO$ interactions of 2.621–2.624 Å and $MeO\cdots CHO$ interactions of 2.528–2.584 Å were observed with the $O\cdots C$ vector making angles of 105.3–133.7° with the carbonyl bond. The lack of a competing conjugation with the framework for the electrophilic group is a favourable factor compared to the use of *peri*-naphthalene systems.

Introduction

Peri-disubstituted naphthalenes have been used extensively for investigating the interactions between pairs of substituents, *e.g.* hydrogen bonding in the “proton sponge” cations **1** and interactions of dimethylamino groups with a wide range of functionalities including Al, Si and Se centred groups *e.g.* in **2–4**.² *Peri*-naphthalene systems have also been used for the investigation of (1,5) nucleophile/electrophile interactions between the common functional groups in organic chemistry *e.g.* involving $-NMe_2$, $-OMe$ or $-SMe$ as the nucleophile and carbonyl based groups³ or electron deficient alkenes as the electrophile, *e.g.* **5–8**.^{4–6} For the more reactive dimethylamino group, a significant degree of bond formation with very reactive electrophilic centres to form zwitterionic structures such as **9** has been observed.^{4,6} Charge density measurements by X-ray crystallography and topological analysis of the total electron density are now being used to probe more deeply interactions that are mediated by the valence electrons. Following this approach a very detailed study of salts of proton sponges such as **1** and its free base have been reported by Mallinson and Wozniak *et al.*,⁷ as well as the study of a nucleophile/electrophile system.⁸



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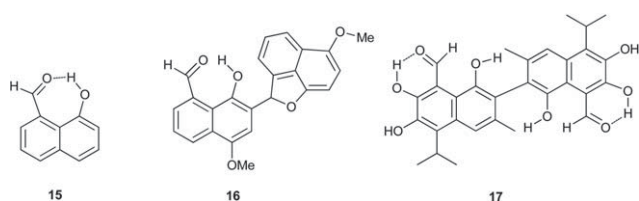
† CCDC reference numbers 837139–837143. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce05955f

Schiemenz has proposed other approaches to estimating the bond formation between a dimethylamino group and a *peri* substituent based on (a) the molecular geometry of the dimethylamino group² and (b) the one bond coupling constant between ^{13}C and 1H in the methyl group.⁹ A greater degree of pyramidalicity at the nitrogen atom or an increase in the ^{13}C , 1H coupling constant in the N-methyl group indicate a greater

degree of bond formation. Akiba has investigated *peri* interactions in trisubstituted anthracene systems, for example between two dimethylamino groups and a boron or ester group lying between them, or between two methoxy groups and a carbocationic centre or an allene derivative containing formally penta- or hexa-coordinate carbon.¹⁰ The 2,2'-disubstituted biphenyl system has also been used to investigate (1,6) molecular interactions where the substituents are no longer constrained to be near one another.¹¹

The success of the *peri*-naphthalene system for observing such interactions is dependent on whether the interaction is sufficient to overcome the tendency of the functional group, especially the electrophilic one, to conjugate with the naphthalene ring system, especially when there is no large 1,6 steric interaction between the electrophilic group with the *ortho* H atom. Thus, in the molecules **10** and **11** containing a methoxy or methylthio *peri* group, X-ray crystallography shows the substituent's electrophilic alkene bond makes a torsion angle of only 46.2 or 36.4° with the aromatic ring's carbon-carbon bond to the *ortho* position.^{5,12} This is in contrast to the corresponding cases where a more reactive dimethylamino group is the nucleophilic centre (**5** and **6**) and where this angle is 56.5 and 50.5°. In naphthalenes **12–14** the *peri*-interaction with the aldehyde group is insufficient to overcome the tendency of the carbonyl group to conjugate with the ring and the C=O/ring torsion angles are only 11–31°. Another issue is that for a nucleophile of type –X–H, where X is a heteroatom, hydrogen bonding between the two *peri* groups may take place.

The deficiency of the *peri*-naphthalene system as a model system for observing nucleophile/electrophile interactions involving hydroxyl groups is illustrated rather well by the crystal structures of **15** and **16** in which the *peri*-related hydroxyl and aldehyde group lie in the naphthalene plane and are splayed apart, presumably so that a hydrogen bond can form between the two groups. Although the hydroxyl hydrogen atom was not unambiguously located in either case, the *peri*-groups are clearly splayed apart. Thus, the OH group is splayed out by 4–6° and the CHO splayed in the opposite direction by 8–11°, with (H)O...O(=C) contact distances of 2.51–2.54 Å consistent with an internal hydrogen bond in **15** and **16** respectively forming a seven-membered ring.^{17,18} There is a large family of clathrates from gossypol **17**¹⁹ in the Cambridge Structural Database²⁰ which contain a *peri* aldehyde group but with both *peri* and *ortho* hydroxyl groups. The ninety observations prefer to show an internal hydrogen bond from the aldehyde to the *ortho* hydroxyl group forming a six-membered ring, which leaves the aldehyde group in the aromatic plane and with the *peri* hydroxyl group oriented so as to direct an sp² type lone pair towards the aldehyde hydrogen atom (Fig. 1). The mean HO...H(C=O) distance is 2.04 Å and suggestive of an attractive interaction.



Thus, we decided to investigate the triptycene ring system **18** as an alternative scaffold for examining (1,5) interactions, with

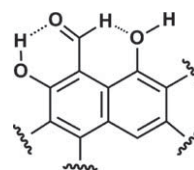
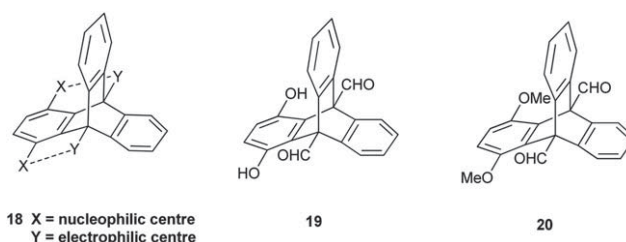


Fig. 1 Relative orientation of the aldehyde and flanking hydroxyl groups in gossypol clathrates.

electrophilic groups located on the sp³ carbon atoms, so that they cannot be involved in conjugation, and so therefore fully available for interaction with electron rich centres at the 1- and 4-positions. As a first step we have investigated the interactions between hydroxyl or methoxy groups with aldehyde groups in compounds **19** and **20**. Prior to our studies, Oki *et al.* used the relative population of rotamers, determined by NMR spectrometry, in 1,9-disubstituted triptycene derivatives to investigate 1,6 molecular interactions *e.g.* between a 1-methoxy or -chloro group and the carbonyl function of a 9-formylmethyl group, as well as in models for S_N2 reactions involving a 1-methoxy and a 9-chloromethyl group.¹⁴ The triptycene system has also been used recently by Gung *et al.* for examining π–π stacking between aromatic groups¹⁵ and interactions between methoxy or C–H groups and aromatic π systems.¹⁶



Discussion

Triptycenes **19** and **20**

The triptycene systems **19** and **20** which contain two pairs of potential interactions between hydroxy or methoxy groups and aldehydes were prepared in several steps from anthracene as published by two of us earlier.²¹ The bis(acetal) of anthracene-9,10-dicarbaldehyde **21** undergoes a Diels–Alder reaction with benzoquinone to give the sterically crowded adduct **22** which contain a fragment which is the diketo tautomer of a quinol. Treatment with acid tautomerises this grouping to the quinol and also deprotects the two aldehyde groups to yield 1,4-dihydroxy-triptycene-9,10-dicarbaldehyde **19**. Treatment with methyl iodide converts **19** to the dimethoxy compound **20**. Slow evaporation of solutions of the 1,4-dihydroxy-triptycene derivative **19** in acetonitrile or ethyl acetate gave two crystalline solvates, whose structures were determined by X-ray crystallography at 120 K and 150 K respectively. The acetonitrile solvate was well ordered, but the second solvate contains channels running through the structure which contain ethyl acetate molecules which are not well ordered with respect to the rest of the structure. The molecular structure and crystal packing for **19**·CH₃CN are shown in Fig. 2–5, with selected geometry in Table 1. The

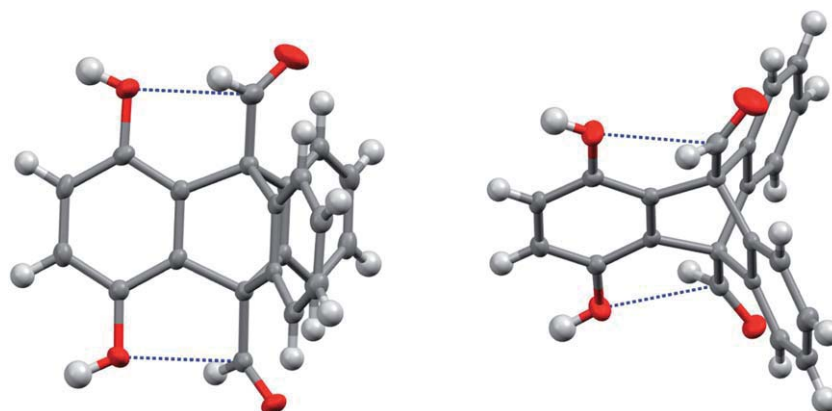


Fig. 2 Two views of the molecular structure of **19** in **19**·CH₃CN drawn with anisotropic displacement parameters at the 50% level.^{27,29}

crystal system is triclinic and the space group $P\bar{1}$. Most notable is the HO \cdots C=O interaction between the functional groups on both edges of the triptycene system. The hydroxyl groups lie in the plane of the attached benzene ring with their sp² lone pair directed towards the carbonyl group. The O \cdots C separations are 2.621(2) and 2.679(2) Å, well within the sum of van der Waals radii (*ca* 3.2 Å), and the aldehyde groups are oriented so that the O \cdots C=O angles are 120.07(13) and 124.72(15)°. The C–OH bonds are tilted slightly towards their respective carbonyl group neighbours by 1.6–1.7°. The plane of each aldehyde group lies quite close to the plane of one unsubstituted benzene ring so that there are contacts from the aldehyde O atoms to *ortho* H atoms of 2.38 and 2.35 Å. The carbonyl bonds make torsions of 15.5 and 18.3° with the respective bond from the adjacent sp³ C to this benzene ring. The aldehyde planes lie as 75.7–77.7° to the other unsubstituted benzene ring, and there is a contact of 2.48 Å from the *ortho* H atom to the carbonyl C atom in both cases, with the H \cdots C vectors lying at 101.8 and 99.3° to the carbonyl group. The exocyclic angles at the two sp³ C atoms of the framework are not symmetrical and are related to the disposition of the carbonyl group with respect to the two adjacent *ortho* H atoms. The largest angle (119.3 and 118.3°) acts to widen the separation between the carbonyl O atom and the nearer *ortho* H atom, and the smallest angle (both 107.5°) relates to the deflection of the plane of the carbonyl group towards the other *ortho* H atom. The

third angle is involved in the O \cdots C=O interaction (113.7 and 114.4°). The endocyclic angles at this carbon lie in the range 104.17–106.30°.

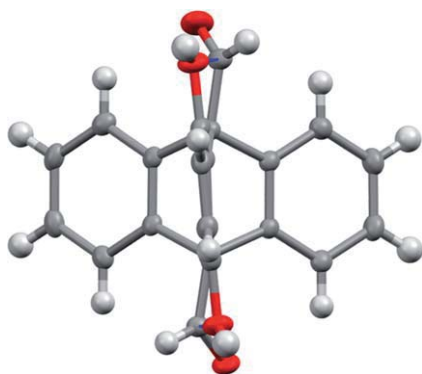
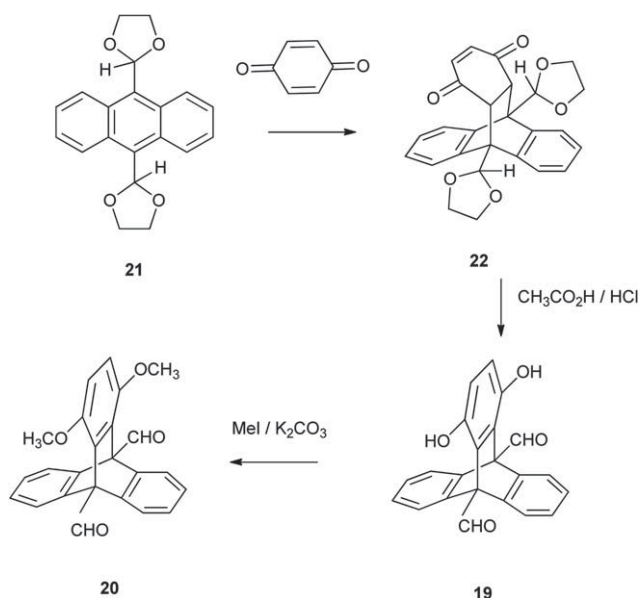


Fig. 3 Molecular structure of **19** in **19**·CH₃CN viewed through the plane of the disubstituted benzene ring, drawn with anisotropic displacement parameters at the 50% level.^{27,29}

The molecules are packed in layers with two of the three benzene rings lying face to face with other benzene rings, and with pairs of centrosymmetrically related acetonitrile molecules lying in pockets between the molecules of **19** (Fig. 4). One carbonyl group is involved in hydrogen bonding to a hydroxyl group in the next layer with close to linear geometry at the H atom. The O \cdots O and O \cdots H distances are 2.831(2) and 1.96(3) Å, with an angle at the H atom of 170.4° and at the carbonyl O atom of 158.0°. The second hydroxyl group makes a hydrogen bond to an acetonitrile molecule (O \cdots N: 2.824(2) Å, N \cdots H: 1.91(2) Å), with angles at the H and N atoms of 175.0 and 138.8° respectively (Fig. 5). It is interesting to note that the carbonyl group which is hydrogen bonded makes a shorter intramolecular contact to its neighbouring hydroxyl group (O=C \cdots OH: 2.621 Å) than the one which is not (by 0.058 Å) and has a longer carbonyl double bond (by 0.022 Å), which would be consistent with the polarizing effect of hydrogen bonding on the π electron cloud of the double bond.

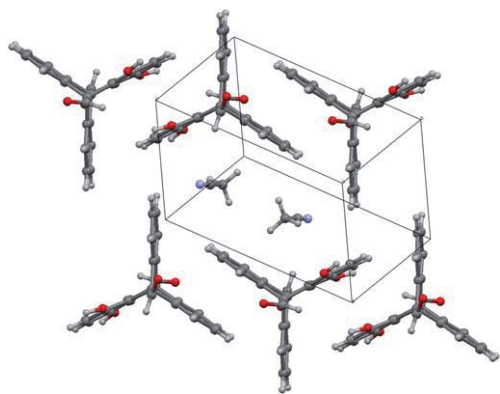


Fig. 4 Crystal packing of **19**·CH₃CN showing location of solvent molecules in pockets between the triptycene molecules, drawn in 'ball and stick' mode.²⁷

The crystal structure of the ethyl acetate solvate of triptycene **19** contains channels running through successive layers of molecules of **19** which contain ethyl acetate that are not ordered with respect to the rest of the crystal structure. The final structure reported here is after the application of the PLATON/SQUEEZE program²² to remove the solvent's electron density from the final model. The crystal system is triclinic, and space group is *P* $\bar{1}$. The accuracy of the structure is lower than that of the other solvate, and some of the errors in the model are absorbed into the anisotropic displacement parameters, particularly the carbonyl O atoms and the unsubstituted benzene rings.

Nevertheless, it is clear that the conformation of triptycene **19** is similar to that in the acetonitrile solvate, showing HO \cdots C=O interactions. In contrast to the acetonitrile solvate, both carbonyl groups are hydrogen bonded to hydroxyl groups of other molecules of **19**. The molecular structure and crystal packing arrangement are shown in Fig. 6. The HO \cdots C=O contacts are 2.664(5) and 2.654(4) Å, and the O \cdots C O \cdots C vector makes angles of 126.3(2) and 133.7(3)° with the carbonyl bond. Each aldehyde group makes a torsion of 38.5 or 23.3° with the bond from the adjacent sp³ carbon atom to the nearest benzene ring, and the contacts between the carbonyl O atoms and the *ortho* H atoms are 2.56 and 2.41 Å. A further geometric analysis^{23,24} of the packing arrangements exhibited by the two different solvates of triptycene **19** revealed a one dimensional similarity along [010] as shown in Fig. 7.

Crystals of the dimethoxy-triptycene derivative **20** were grown from DCM. The crystal system is monoclinic and the space group is *Pa* with two unique molecules in the asymmetric unit and thus four crystallographically unique MeO \cdots C=O interactions. The two molecules are illustrated in Fig. 8 and the packing arrangement is shown in Fig. 9. The overall geometries of the four interactions are similar, though the influences of other packing effects leads to some variations. Each of the methoxy groups lies close or reasonably close to the plane of the attached aromatic ring, so that it directs an sp² type lone pair towards the carbon atom of a carbonyl group at a bridgehead position. The aldehyde groups are oriented so that the (Me)O \cdots C=O angles lie in the range 105.24–114.60°, and each aldehyde group lies close

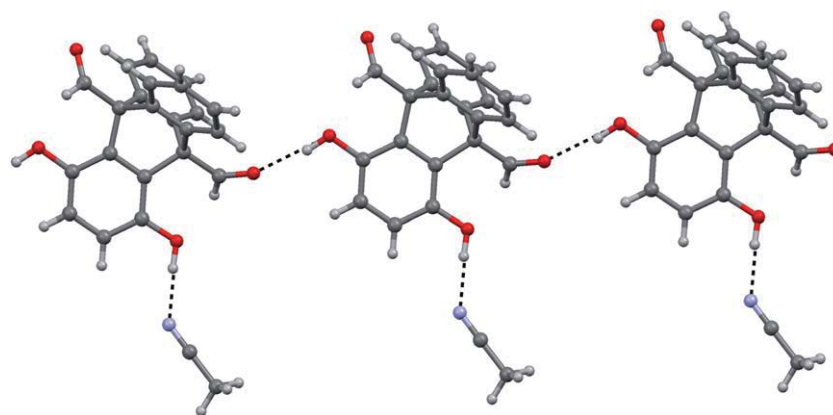


Fig. 5 Hydrogen bonding pattern in crystal structure of **19**·CH₃CN drawn in 'ball and stick' mode.²⁷

Table 1 Geometric details of O \cdots C=O interactions

Compound	O \cdots C(=O)/Å	O \cdots C=O Angle/°	C=O/Å	O \cdots H(<i>ortho</i>)/Å	Torsion O=C(sp ³)-C(benzene)	C=O \cdots HO/Å
19 ·CH ₃ CN	2.621(2)	120.07(13)	1.209(2)	2.38	15.5(3)	1.96
	2.679(2)	124.72(15)	1.187(2)	2.35	18.3(3)	—
19 ·EtOAc ^a	2.664(5)	133.7(3)	1.089(4)	2.56	38.5(6)	2.03
	2.654(4)	126.3(2)	1.189(3)	2.41	23.3(5)	2.02
20	2.534(9)	105.3(5)	1.190(9)	2.28	11.9(11)	—
	2.542(8)	113.9(5)	1.197(7)	2.30	3.6(10)	—
	2.584(9)	114.6(5)	1.203(8)	2.36	7.3(10)	—
	2.528(9)	111.5(5)	1.210(8)	2.32	6.9(11)	—

^a The disordered solvent was excluded from this structural model using the PLATON/SQUEEZE program.

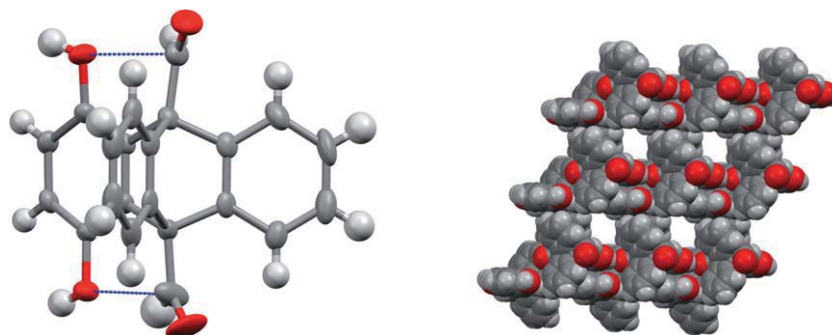


Fig. 6 Crystal structure of **19**.CH₃CO₂C₂H₅ (a) showing a single molecule with anisotropic displacement parameters drawn at the 50% level, (b) showing the channels running along the *a* axis between molecules of **19** (drawn in space filling mode) which are filled with ethyl acetate molecules (not shown).²⁷

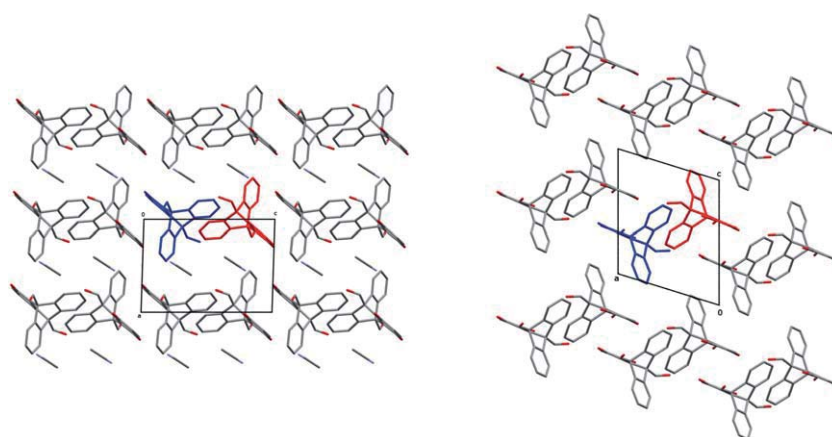


Fig. 7 Crystal packing of the two different solvates of **19**, showing one dimensional similarity along [010].

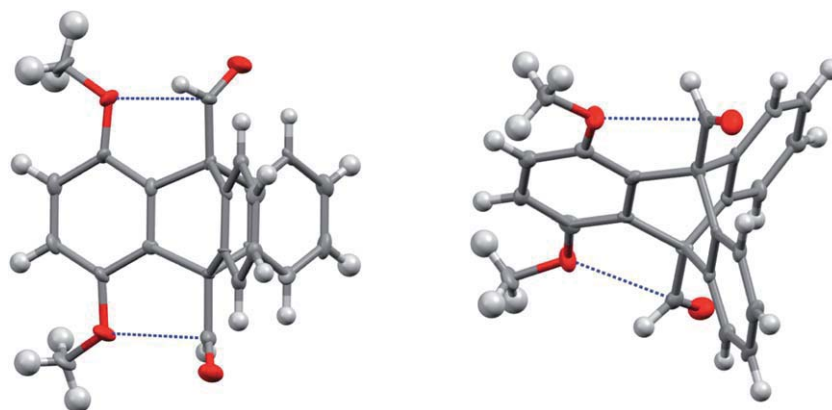


Fig. 8 Structures of the two independent molecules of **20** with the anisotropic displacement parameters drawn at the 50% level.^{27,29}

to the plane of another of benzene ring. The O...C separations shown by the four interacting pairs lie in the range 2.528(9)–2.584 (9) Å with an average value of 2.547 Å. Full details of the molecular geometries of the four interactions are given in Table 1. The range of variation between the interaction geometries is illustrated by the torsion angle between the C–O bond of the methoxy group and the nearest aromatic C,C bond which varies from 4.3 to 22.4°. The orientation of the aldehyde group close to

the plane of an unsubstituted benzene ring leads to short (1,6) O...H contacts between the carbonyl O atom and an *ortho* aromatic H atom (2.28–2.36 Å). The methoxy groups are displaced towards the carbonyl groups due to the steric interaction between the methyl group and an *ortho* H atom, with the C (aryl)–OMe bond displaced by 3.7–4.5° from the symmetrical position. The two independent molecules of **20** pack in separate layers perpendicular to the *c* axis.

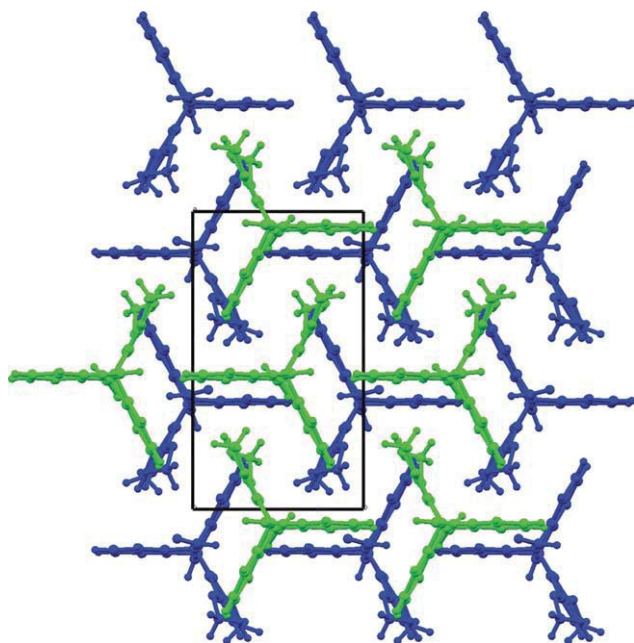


Fig. 9 Crystal packing arrangement of **20** showing packing of the two independent molecules of **20** (blue and green) in layers perpendicular to the *c* axis.

Diels–Alder adduct **22**

The Diels Alder adduct **22** between benzoquinone and the anthracene bis(acetal) **21** is a particularly interesting molecule, since firstly solution NMR suggests it is a tautomer of a quinol derivative and secondly there are likely to be interactions between the adjacent carbonyl and acetal groups. Hence the crystal structure was determined by X-ray diffraction at 100 K. The molecular structure is shown in Fig. 10. The molecule is most notable for the lengths of the two C–C bonds which are formed on addition of the benzoquinone to the anthracene: 1.5841(19) and 1.5894(19) Å, *ca* 0.04–0.05 Å longer than the standard sp³C–sp³C bond. Furthermore, the bond joining these two bonds, which had played the part of the dienophile in the Diels Alder reaction, is also strained and is 1.5597(19) Å long. The two dioxolane rings adopt envelope conformations with an O atom at the flap, but adopt different staggered conformations with respect to the rest of the molecule, with either a C–O bond or a C–H bond lying *anti* to the quinone grouping. There are steric interactions between the pairs of carbonyl and dioxolane groups,

which are somewhat mitigated by the pair of particularly long C–C bonds. The quinone ring is flexed to move the keto O atoms away from the dioxolane substituents, and the keto O atoms lie 1.367 and 0.685 Å out of the plane of the four non-carbonyl carbon atoms of the ring. The considerable difference in these values is related to the quite different interactions they make with their adjacent dioxolane rings. In the former case, the interaction between carbonyl and dioxolane groups involves an acetal O atom making a short contact with the carbonyl carbon of the ketone (2.669 Å) which may be attractive in nature, while in the other case, the shortest contact in the interaction is a 1,6 contact between the carbonyl O atom and the methine H atom of the dioxolane ring (2.35 Å). In this way too, repulsive interactions between keto and dioxolane oxygen atoms are minimized by keeping them more than 3 Å apart.

Conclusion

The triptycene skeleton has been demonstrated to be a useful scaffold for investigating (1,5) interactions between functional groups. A particular advantage is that the group located on the central sp³ carbon atom cannot conjugate with the framework as happens in some *peri*-naphthalene systems. The use of the triptycene skeleton has the potential for extension further towards systems where partial bond formation may take place, depending on the reactivities of the groups chosen and on the installation of *ortho* substituents to create increased steric pressure. Further work in this direction is underway.

Experimental

X-Ray crystallographic measurements were made on Nonius KappaCCD area-detector diffractometer located at the window of a Nonius FR591 rotating-anode X-ray generator, equipped with a molybdenum target ($\lambda_{\text{Mo-K}\alpha} = 0.71073$ Å). (for **19**.acetonitrile and **20**) or a Bruker KAPPA APEX II CCD diffractometer equipped with an Oxford Cryosystems low temperature device (for **19**.ethyl acetate and **22**). Structures were solved and refined with the SHELXS and SHELXL suites²⁵ using the XSEED²⁶ interface.

Crystal data for **19**.CH₃CN: C₂₂H₁₄O₄.C₂H₃N, *M_r* = 383.39, triclinic, *P* $\bar{1}$, *a* = 9.0118(3), *b* = 9.6549(4), *c* = 11.6967(5) Å, α = 80.718(3), β = 87.782(3), γ = 65.542(2)°, *V* = 913.81(6) Å³, *Z* = 2, *D_{calc}* = 1.39 g cm^{−3}, *T* = 120 K, μ = 0.095 mm^{−1}, *F*(000) = 400, 4190 unique reflections (*R_{int}* = 0.0588), 2991 with *I* > 2σ(*I*), max. (sin θ)/λ = 0.65 Å^{−1}, final *R*₁ = 0.055, *wR*₂ = 0.13.

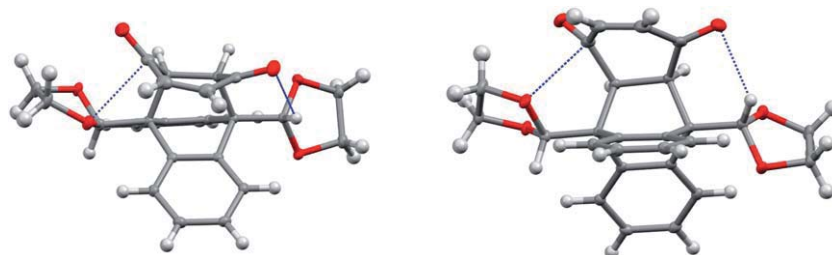


Fig. 10 Molecular structure of **22** showing the distorted dihydroquinone ring (left) and the two short contacts (O⋯C=O and C=O⋯H–C) between a ketal group and a carbonyl of the dihydroquinone (right).^{27,29}

Crystal data for **19**. $0.75\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$: $\text{C}_{22}\text{H}_{14}\text{O}_4 \cdot 0.75\text{-C}_4\text{H}_8\text{O}_2$, $M_r = 408.4$, triclinic, $P\bar{1}$, $a = 9.3754(7)$, $b = 9.6285(7)$, $c = 11.4470(9)$ Å, $\alpha = 69.585(4)$, $\beta = 69.800(4)$, $\gamma = 77.586(4)^\circ$, $V = 903.60(12)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.50$ g cm⁻³, $T = 150$ K, $\mu = 0.106$ mm⁻¹, $F(000) = 428$, 4462 unique reflections ($R_{\text{int}} = 0.0455$), 2208 with $I > 2\sigma(I)$, max. $(\sin \theta)/\lambda = 0.67$ Å⁻¹, final $R_1 = 0.070$, $wR_2 = 0.18$. The final structure refinements were done after application of the PLATON/SQUEEZE program to exclude the channels of ethyl acetate from the model.

Crystal data for **20**. $\text{C}_{24}\text{H}_{18}\text{O}_4$, $M_r = 370.38$, monoclinic, Pa , $a = 14.0278(3)$, $b = 7.9798(2)$, $c = 15.6964(4)$ Å, $\beta = 96.197(2)^\circ$, $V = 1746.77(7)$ Å³, $Z = 4$, $D_{\text{calc.}} = 1.41$ g cm⁻³, $T = 120$ K, $\mu = 0.096$ mm⁻¹, $F(000) = 776$, 3991 unique reflections, 2985 with $I > 2\sigma(I)$, max. $(\sin \theta)/\lambda = 0.65$ Å⁻¹, final $R_1 = 0.062$, $wR_2 = 0.013$. The crystal was refined as a nonmerohedral twin with two component ratio 0.52 : 0.48.

Crystal data for **22**. $\text{C}_{26}\text{H}_{22}\text{O}_6$, $M_r = 430.44$, monoclinic, $C2/c$, $a = 21.837(2)$, $b = 9.297(1)$, $c = 19.231(2)$ Å, $\beta = 100.008(3)^\circ$, $V = 3845.0(7)$ Å³, $Z = 8$, $D_{\text{calc.}} = 1.49$ g cm⁻³, $T = 100$ K, $\mu = 0.106$ mm⁻¹, $F(000) = 1808$, 4773 unique reflections ($R_{\text{int}} = 0.0335$), 3746 with $I > 2\sigma(I)$, max. $(\sin \theta)/\lambda = 0.67$ Å⁻¹, final $R_1 = 0.043$, $wR_2 = 0.11$.

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